STUDIES ON HALOGEN SUBSTITUTIONS

A THESIS

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SUMMARY

In this desertation the following subjects are investigated :

I) Chlorination and bromination of some aromatic compounds.

II) Attempted fluorination of some highly chlorinated aromatic acids and their derivatives.

III) Preparation of some highly halogenated lactones, oxazolones and arylidene phthalides.

I) Chlorination and bromination of some aromatic compounds is affected by means of chlorine and bromine in fuming sulphuric acid in the presence of iodine as a halogen carrier. According to the products obtained, the different compounds tested in this investigation are classified into

(i) Compounds that undergo chlorination and bromination with chlorinolysis and brominolysis of the groups present with the formation of hexachlorobenzene ([illegible]) in case of chlorination and hexabromobenzene (XCI) or pentabromochlorobenzene (XC) in case of bromination (cf. Table 1, page 83).

(ii) Compounds that undergo both halogenation and oxidation with the formation of chloranil (VI) in case of chlorination and bromanil (LV) in case of bromination (cf. Table 2, page 83).

(iii) Compounds that undergo halogenation without removal of the groups present.

This method of halogenation is not suitable for polynuclear aromatic hydrocarbons due to the formation of water soluble sulphonic acids.

With respect to the formation of chloranil (VI) and bromanil (LV) the different groups are classified into :

(a) Inhibitory groups : which prevent the formation of chloranil and bromanil such as : -CHO, -COOH, -CN, -COCl, and halogen atoms.

(b) Promotor groups: which favour the formation of chloranil and bromanil such as : -OH, $-OCH_3$, NO_2 groups.

II Attempted fluorination of some highly chlorinated aromatic acids was affected by means of anhydrous potassium fluoride in N-methyl-pyrrolidone as a polar solvent.

Fluorination of tetrachlorophthalic acid, [illegible] and gave a very small yield of 1,2,3,4-tetrachlorobenzene (XCIII) (cf. page 88). Also fluorination of tetrachloroterephthalic acid gave little yield of 1,2,4,5-tetrachlorobenzene (XCV) (cf. page 89).

The two isomeric tetrachlorobenzenes (XCIII) and (XCV) were nitrated to the corresponding dinitrotetrachlorobenzenes.

III Preparation of some halogenated lactones, oxazolones, and arylidene phthalides.

Tetrachloro amd tetrabromophthalic anhydrides condense with β-benzoylpropionic acid in acetic anhydride-sodium acetate mixture to give α-tetrachlorophthalal-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (CIIa) and α-tetrabromophthalal-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (CIIb) respectively (cf. page 93).

The condensation of tetrachloro and tetrabromophthalic anhydrides with hippuric acid under the same conditions give 2-phenyl-4-tetrachlorophthalal-5-oxazolone (CIIIa) and 2-phenyl-4-tetrabromophthalal-5-oxazolone (CIIIb) respectively (cf. page 94).

The tetrachlorolactone (CIIa) and the tetrachlorooxazolone (CIIIa) react with hydrazine hydrate in alcohol to give 3,4,5,6-tetrachloro-N-aminophthalimide (CIV) (cf. page 95). The reaction of the tetrabromoanalogues (CIIb) and (CIIIb) with hydrazine hydrate, also give 3,4,5,6-tetrabromo-N-aminophthalimide (CVI) (cf. page 98).

Benzylamine reacts with the tetrachlorolactone and oxazolone to give N-benzyl tetrachlorophthalamide (CVIIa). The reaction of the tetrabromoanalogues with benzylamine also gives N-benzyl-tetrabromophthalamide (CVIIb) (cf. page 99).

Benzaldehyde, anisaldehyde, and p-chlorobenzaldehyde condense with 3,4,5,6-tetrachlorophthalide (CVIII) in the presence of piperidene to give the corresponding arylidene phthalides (CIX) (cf. page 102).

These arylidene phthalides (CIX) were converted to the corresponding diones (CX) (cf. page 103) by means of sodium methoxide.

Hydrazine hydrate reacts with the arylidene phthalides (CIX) to give comound to which structure (CXI) (cf. page 104) was assigned.

CHAPTER I

INTRODUCTION

SOME ASPECTS OF AROMATIC HALOGENATION[1]

In analogy with aromatic nitration, we would expect the most effective species in aromatic halogenations to be the electron - deficient halogenonium ions, $:\underset{\cdot\cdot}{Cl}^{+}:$, $:\underset{\cdot\cdot}{Br}^{+}:$, $:\underset{\cdot\cdot}{I}^{+}:$. Aromatic brominations and chlorinations are ordinarily carried out using elemental bromine or chlorine, often in the presence of a Lewis acid such as anhydrous zinc chloride, aluminium chloride, or ferric chloride.

It had been suggested by some authors[2] that the function of such an acid is the heterolysis of the halogen molecule for example :

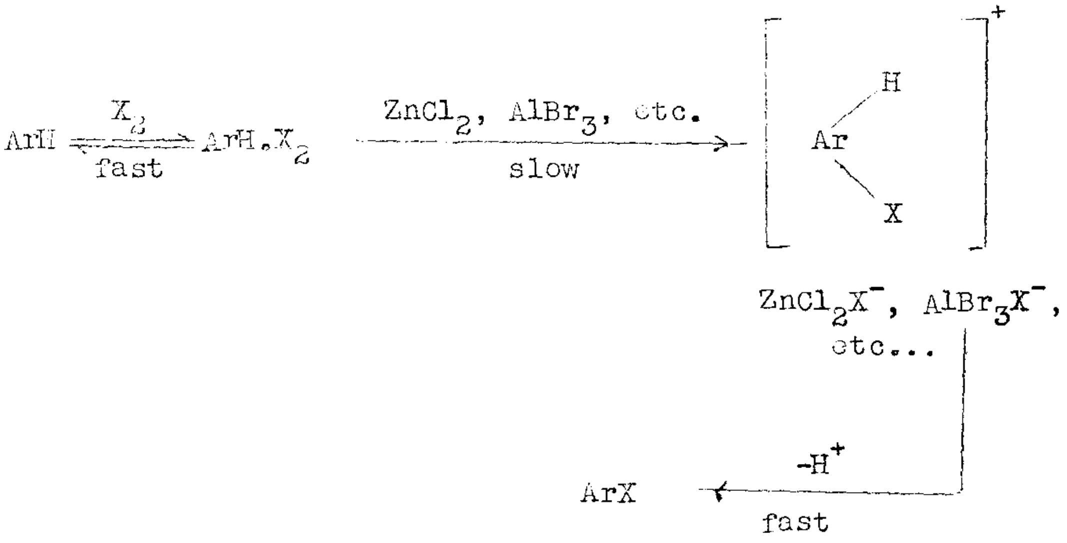
$$Br_2 + ZnCl_2 \rightleftharpoons Br^{+} + ZnCl_2Br^{-} ,$$

such heterolysis occurs prior to the attack on the substrate. However, there seems little, if any, reliable evidence that such a heterolysis takes place at ordinary temperatures, and it is far more likely that the attacking species is the diatomic halogen molecule itself.

If this is the case, the Lewis acid must await the formation of a complex between substrate and halogen

[illegible]
[illegible] atoms.

At present, then, the most likely mechanism for such halogenations appears to be :



in which the rate-determining step is a simultaneous nucleophilic "Push" by the substrate and an electrophilic "Pull" by the catalyst on opposite ends of the halogen molecule with heterolytic breakage of the X - X bond.

Recent kinetic studies[3a,b,c] of such halogenations are consistent with this mechanism, for there appear to be no cases where a halogenation of this sort has a zero

[illegible]

Interhalogens, such as I-Cl[4a] and I-Br[3b] and iodine itself[4b] may act in a similar capacity. It should be clear that a halogenonium ion, X^+, when it can be generated is a more powerful halogenating agent than the corresponding halogen molecule, X_2 , since halogenation with the latter requires an extra activation energy to break the X - X bond.

Elemental iodine is a less powerful halogenating agent than are chlorine and bromine, for the metal halides, usually used as halogenation catalysts, co-ordinate only weakly with iodine, and their "pulling power" is of little value.

Virtually nothing of what had been said regarding chlorination, bromination, or iodination may be applied to fluorination; for it is certain now that the reactions of elemental fluorine with aromatic compounds, except perhaps at very low temperatures, proceed through free fluorine atoms, formed in a preliminary homolytic cleavage of F_2 molecules.[5] The very low F - F bond energy (about 37.0 k.cal. per mole), favours conversion of F_2 into atoms; whereas the very high ionization potential of the fluorine atom (about 100 k.cal. per mole) renders the formation of the $:\underset{..}{F}^{+}:$ ion in chemical systems impossible.